

Catalyst Transformation During Alkali-Catalyzed Carbon Gasification

F. Shadman, W.A. Punjak and D.A. Sams

Department of Chemical Engineering, University of Arizona
Tucson, Arizona 85721

The kinetics and mechanism of carbon gasification reaction catalyzed by alkali metals have been the subject of numerous studies and comprehensive reviews are available (1-4). Although the mechanism of catalyst action is not completely understood, there is a general agreement that the reaction follows a redox mechanism (5-6). In this mechanism, the alkali catalyst cycles between an oxidized and a reduced form. During this cycle the catalyst transfers oxygen from the gaseous reactant to the carbon surface; the net effect is production of CO. Presently, the disagreement is on the nature and the stoichiometry of the catalytic intermediate compounds. The purpose of this study is to characterize the mechanism and the kinetics of the processes in which sodium and potassium carbonates are reduced from their initial forms to the catalytic intermediate forms.

EXPERIMENTAL METHOD

Carbopack B (by Supelco) was used as the high purity carbon substrate. Catalyst in the initial form of sodium or potassium carbonate was applied by the incipient wetting technique. The catalyst/carbon ratio was controlled by varying the alkali concentration in the impregnation solution. Atomic emission spectroscopy was used to analyze the samples for alkali content. The catalyst type and concentration of the samples used in this study are given in Table 1.

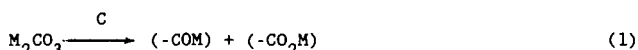
Two reactor systems were used in the course of this study. The first utilized a small differential reactor for quick response times while the second used an electronic microbalance for direct measurement of sample weight. Both systems included a movable furnace which allowed rapid heating and cooling or programmed temperature change in the reactor. The details of experimental set-up are given elsewhere (7,10).

For each run, 25-30 mg of the impregnated carbon was loaded into the reactor. The reactor was then purged with Ultra high purity nitrogen to remove the oxygen before heating the sample. The experiments were conducted under Temperature and Concentration Programmed Reaction (TCPR) conditions. Three schedules of programmed conditions were used. In Schedule 1 (Fig. 1), the samples were rapidly heated to 800°C under nitrogen. After complete evolution of H₂O, CO₂ and CO, the samples were cooled rapidly and removed for analysis. Schedule 2 (Fig. 2) was similar except the samples were

quenched before complete catalyst reduction to determine the relationship between CO evolution and catalyst loss. In Schedule 3, (Fig. 3) the partial reduction under nitrogen was followed by gasification under a mixture of 15% CO₂ in nitrogen. After a short gasification stage to measure the gasification rate, the samples were quenched and removed for analysis.

RESULTS AND DISCUSSION

In an earlier study (11), a mechanism was suggested for the interaction between carbon and potassium carbonate under inert conditions above 700°C. This mechanism, which is expected to hold for both sodium and potassium carbonates, can be written in the following general form:



This mechanism allows for the sequential reduction of the catalyst followed by catalyst vaporization and loss.

In the early stage of the sample heat up, a small CO₂ peak is observed. This peak is due to the decomposition of bicarbonate to carbonate (10,11). During the rest of the reduction stage, carbon monoxide is the only significant gaseous product. Therefore, the time profile of CO is a direct measure of the overall reduction kinetics. The CO profile shown in Figure 1 is a typical profile for initial catalyst loadings above saturation. The CO concentration exhibits a plateau with almost constant CO gasification rate. As the initial loading is decreased, the width of the CO plateau decreases while the rate of CO production does not change significantly. For very low concentrations the profile does not exhibit a plateau. These results indicate that at catalyst loadings greater than what is required for surface saturation, catalyst is the excess reactant and carbon surface is the limiting reactant. Under these conditions, the reduction rate is determined by the carbon substrate area which is independent of catalyst loading. The very small increase in CO across the plateau is due to the increase in carbon surface area caused by conversion. At initial concentrations lower than saturation (initial metal to carbon atomic ratio of about 0.01 for potassium and 0.04 for sodium) the rate of reduction varies with both loading and time and no plateau is observed.

The rise and fall of the CO peak are primarily due to the effect of reaction kinetics and not simply an artifact of the reactor residence time response. Without these effects the rise and fall would have been much sharper. This is because dispersion in the reactor is relatively negligible. The rise is due to the increase in

the concentrations of $(-\text{CO}_2\text{M})$ and $(-\text{COM})$ supplied by reaction 1. The fall is due to the depletion of the carbonate.

The dependence of the average catalyst reduction rate on loading is shown in Figure 4. Total reduction time is a linear function of the initial catalyst loading. This indicates that the average rate is independent of loading as long as the carbon substrate is saturated. The rate will vary with loading for unsaturated samples as indicated by the curvature of the lines at low catalyst loadings. As expected, the shape of the curve indicates that the turnover number (measure of rate per catalyst atom) for an unsaturated surface is higher than that for a saturated surface.

The reduction mechanism suggests that the catalyst is reduced prior to loss by vaporization. To measure the relative rates of catalyst reduction and vaporization, a series of runs were conducted where the samples were removed after various levels of catalyst reduction and analyzed for catalyst content (Schedule 2). The results are shown in Figure 5 and indicate that the catalyst vaporizes rapidly upon complete reduction. This can occur only if reaction 4 is substantially faster than reaction 3.

An important observation is that the rate of catalyst loss is dramatically decreased after all the catalyst is reduced. In other words, the residual catalyst left on the surface at the end of the reduction process is relatively stable. This means that reaction 4 is somehow enhanced by the presence of carbonate. A possible explanation is that the strong attraction of carbonate to carbon sites causes the decomposition of $(-\text{CM})$ and the release of carbon sites which interact with carbonate.

CONCLUSION

The reduction of potassium and sodium carbonates is a prerequisite for the formation of surface catalytic sites, and further reduction of these surface sites is an integral part of the mechanism suggested for catalytic gasification. In addition, the alkali catalyst is lost from a site only after it has been completely reduced.

For a sufficiently high loading, a sodium or potassium impregnated carbon sample subjected to heat under an inert atmosphere will generate a CO concentration/time profile with a distinct plateau region. In this region, catalyst is the excess reactant and carbon surface area is the limiting reactant. For low loading samples, catalyst is the limiting reactant and no plateau is observed. The reduction rate is independent of loading for high loading samples while for low loading samples the rate is a function of both loading and time.

There is a saturation limit for the alkali catalyst on carbon substrates. This limit appears to be the same for both sodium and potassium on molar basis. In general, the surface saturation limit is independent of the initial loading but depends on the total surface area of the substrate.

REFERENCES

1. Wen, W.Y., Catal. Rev.-Sci. Eng., 22(1), 1 (1980).
2. McKee, D.W., Chem. Phys. Carbon, 16, 1 (1981).
3. Wood, B.J. and K.M. Sancier, Catal. Rev.-Sci. Eng., 26(2), 233 (1984).
4. Pullen, J.R., IEA Coal Research, No. ITCIS/TR26 (1984).
5. McKee, D.W., Fuel, 62(2), 170 (1982).
6. Moulijn, J.A., M.B. Gerfontain and F. Kapteijn, Fuel, 63(8), 1043 (1984).
7. Sams, D.A. and F. Shadman, accepted for publication in AIChE J.
8. Sams, D.A., T. Talverdian and F. Shadman, In Press, Fuel (1985).
9. Talverdian, T., "Catalyst Loss During Potassium-Catalyzed CO₂ Gasification of Coal Char and Carbon," M.S. Thesis, University of Arizona (1984).
10. Sams, D.A. "The Kinetics and Mechanism of the Potassium Catalyzed Carbon/Carbon Dioxide Gasification Reaction", Ph.D. Dissertation, University of Arizona (1985).
11. Shadman, F. and Sams, D.A., Proceedings of the 17th Biennial Conference of the American Carbon Society, Lexington, Ky., 182 (1985).

Table 1. Catalyst Specifications in the Studied Samples

Sample	Catalyst	(M/C) _o atomic ratio
A	K	0.00089
B	K	0.0027
C	K	0.0054
D	K	0.013
E	K	0.021
F	K	0.025
G	K	0.027
H	Na	0.011
I	Na	0.029
J	Na	0.049
K	Na	0.067
L	Na	0.091
M	Na	0.131

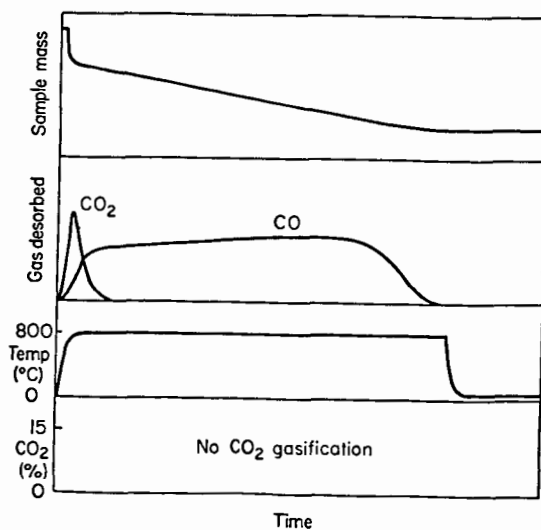


Figure 1. Temperature-programmed reaction; Schedule 1

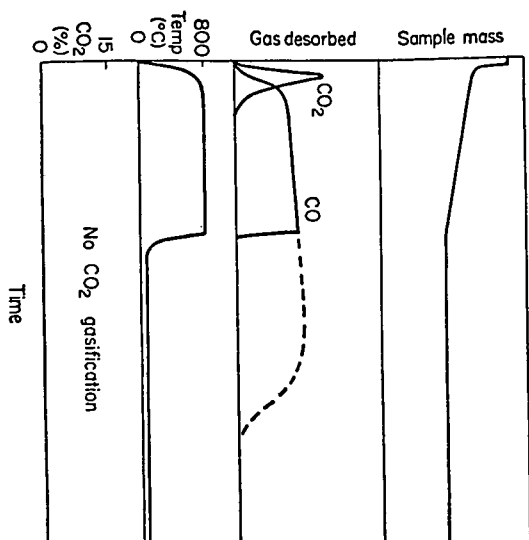


Figure 2. Temperature-programmed reaction; Schedule 2

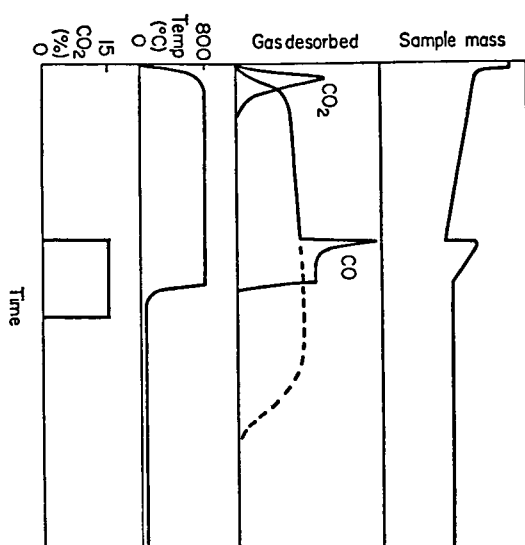


Figure 3. Temperature- and concentration-programmed reaction; Schedule 3

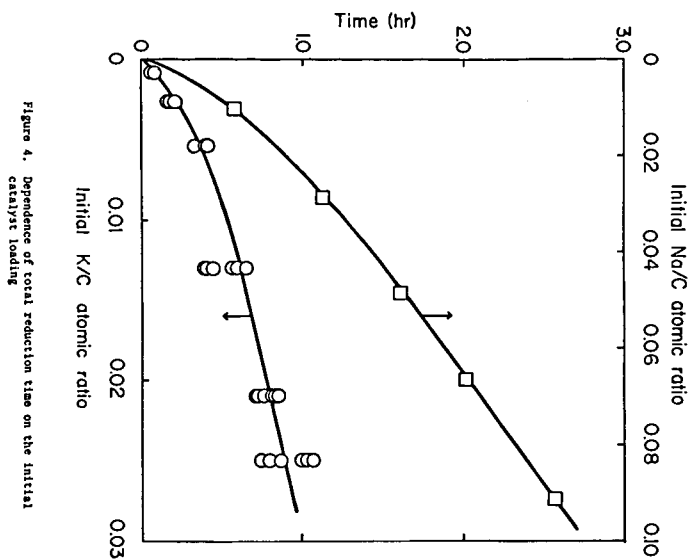


Figure 4. Dependence of total reduction time on the initial catalyst loading

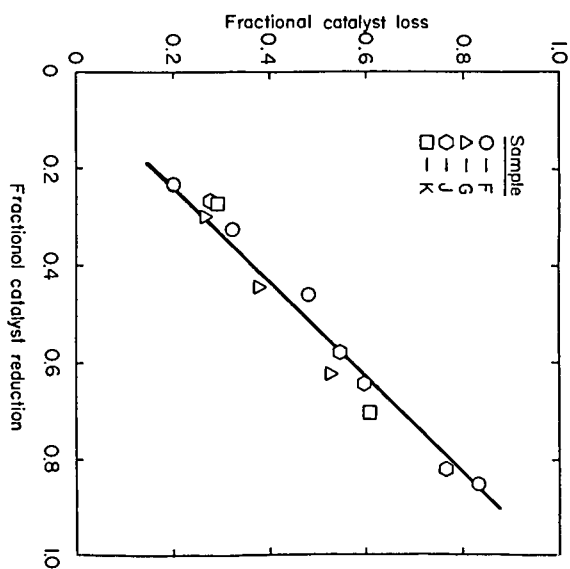


Figure 5. Catalyst loss during reduction